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Source Category Survey
Ammonia Manufacturing Industry

TRW Energy Systems Group
Research Triangle Park, NC

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The report described the ammonia manufacturing industry, the process, emission sources, and available control technology. The domestic ammonia manufacturing industry is entering a sustained period of no growth in production capacity. While there will be an increase in demand for ammonia, particularly in the form of nitrogen fertilizers, the domestic industry has sufficient excess capacity to meet demands at least through 1985. In 1979 a total of 101 synthetic ammonia plants with a rated production capacity of 22.5 Tg (24.8 x 10^6 tons), or 73 percent of capacity. Approximately 75 percent of the ammonia produced in the United States is used as fertilizer, the remaining ammonia is used as a raw material in the manufacture of polymeric resins, explosives, nitric acid, and other products.

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1. EXECUTIVE SUMMARY

1.1 INTRODUCTION

The United States Congress has mandated that the Environmental Protection Agency promulgate new source performance standards for major source categories; a ranking of 59 such sources was recently published in the Federal Register. The standard-setting process involves three principal activities: information gathering, analysis of information, and development of standards. This report comprises the results of the first phase as applied to the ammonia manufacturing industry. The report describes the industry, the process, emission sources, and available control technology.

1.2 INDUSTRY DESCRIPTION

The domestic ammonia manufacturing industry is entering a sustained period of no growth in production capacity. While there will be an increase in demand for ammonia, particularly in the form of nitrogen fertilizers, the domestic industry has sufficient excess capacity to meet demands at least through 1985.

In 1979 a total of 101 synthetic ammonia plants with a rated production capacity of 22.5 Tg (24.8×10^6 tons) per year were reported in 30 states. Production in 1979 was 16.4 Tg (18×10^6 tons), or 73 percent of capacity. Twenty-seven plants were reported idle in March 1980, representing 3.5 Tg (3.9×10^6 tons) of capacity. Currently, the heaviest concentration of production in the United States is in the natural-gas producing states of Texas and Louisiana which contain 17 and 15 sites, respectively. The five states of Texas, Louisiana, California, Iowa, and Oklahoma contain 70 percent of the total production capacity.

Approximately 75 percent of the ammonia produced in the United States is used as fertilizer, either directly as ammonia or indirectly after

synthesis as urea, ammonium nitrate, and monoammonium or diammonium phosphates. The remaining ammonia is used as a raw material in the manufacture of polymeric resins, explosives, nitric acid, and other products.

The production of ammonia increased an average of 2.9 percent annually during the 1970's. This rate was substantially less than in the 1960's when ammonia production increased 165 percent over the decade. Demand for fertilizer is expected to increase at an annual rate of 3 percent through the 1980's. The reserve idle capacity in the United States ammonia industry plus an increase in ammonia imports is expected to meet this demand without new plant expansion. In addition, improvements in facilities can significantly increase production capabilities of existing facilities. Many plants are now able to achieve production rates of 10 percent or more over rated capacities without an increase in emissions. Uncertainty over the price and availability of natural gas would discourage new plant construction even under a more promising demand scenario. Worldwide ammonia production will most likely shift to areas where inexpensive natural gas is available such as Mexico and Trinidad.

A major conclusion of this examination of ammonia production is that the industry is entering a sustained period of no growth. In addition, production of feedstock from coal gasification will not be available in the foreseeable future because of the untested nature of this technology and the high capital investment needed for this change in methods.

1.3 PROCESS DESCRIPTION/EMISSIONS

Ninety-eight percent of the ammonia produced in the United States is by catalytic steam reforming of natural gas. The gas is converted to hydrogen, purified, and reacted with nitrogen to produce ammonia. In consideration of the increasing cost and decreasing availability of natural gas, many have contemplated gasifying coal to produce synthesis gas. This approach would double the cost of an ammonia plant, and would increase energy consumption by 30 percent and necessitate coal handling and preparation as well as ash disposal. Accordingly, the discussion that follows is based on the synthesis of ammonia using natural gas as a feedstock.

1.3.1 Overall Process

Figure 1-1 is a generalized flow diagram of a typical ammonia plant. The production of ammonia from natural gas comprises six major steps:

1. Desulfurization (to prevent poisoning the nickel reformer catalyst)
2. Reforming of CH_4 to H_2 and CO
3. Shifting of CO with H_2O to produce additional H_2
4. Absorption of CO_2
5. Methanation of residual CO_2 prior to NH_3 synthesis
6. Synthesis of NH_3 from H_2 and N_2

1.3.2 Desulfurization

Natural gas contains sulfur in the form of H_2S which must be reduced to below 280 $\mu g/m^3$ to prevent poisoning the nickel reforming catalyst. There are two common desulfurization methods: activated carbon and zinc oxide. Regeneration of carbon is accomplished by passing superheated steam through the bed. Newer plants are tending to use a zinc oxide bed which has basicially three advantages: energy in the form of steam regeneration is not required, there are no air emissions, and higher molecular weight hydrocarbons are not removed (which would reduce the heating value of the gas). Heavy hydrocarbons tend to nullify the effectiveness of the carbon. Also, carbon does not remove carbonyl sulfide. Emission factors for SO_2, CO, and VOC are 6, 6900, and 3600 g/Mg (grams per megagram of ammonia produced), respectively. Based on a nominal 900 Mg per day ammonia plant using carbon desulfurization, annual emissions for SO_2, CO, and VOC are 1.8 Mg, 2100 Mg, and 1100 Mg, respectively. A few plants have installed incinerators, despite the added cost, to combust the CO and VOC. Industry consensus is that new ammonia plants will use zinc oxide rather than activated carbon, which would eliminate the desulfurizer as an emission point.

1.3.3 Catalytic Steam Reforming

Steam reforming proceeds in two steps. In the primary reformer (the radiant section of the reformer), methane reacts with steam in the presence of a nickel catalyst to produce hydrogen and CO_2. Partially reformed gas flows to the refractory-lined secondary reformer where it is mixed with air (the amount of which is fixed by the ultimately-required H_2/N_2 ratio of 3 to 1). Fuel for the primary reformer consists of 7/8 natural gas and 1/8 purge gas from the ammonia synthesizer.

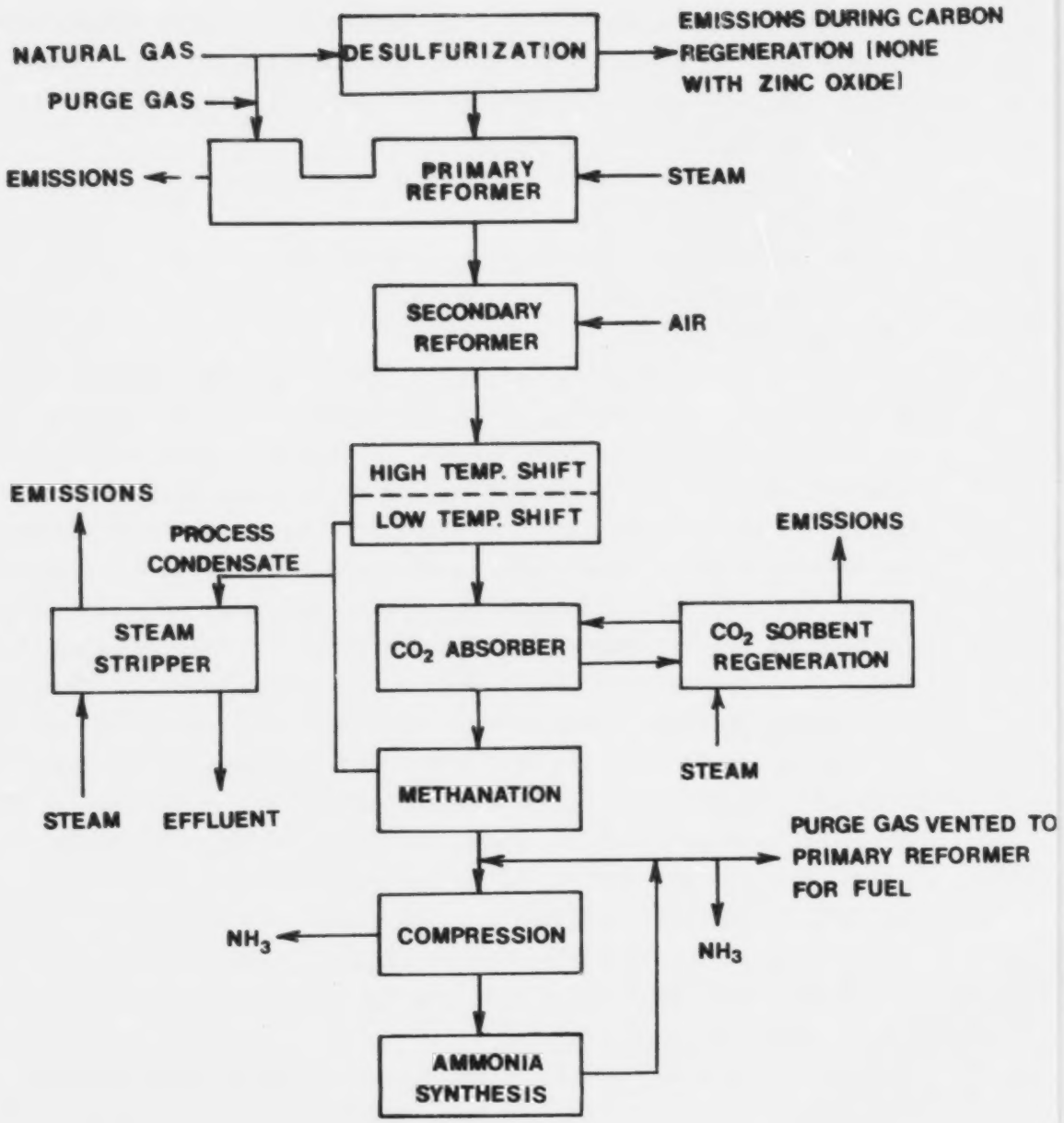

Figure 1-1. Process flow diagram of a typical ammonia plant.

The emission factors for the primary reformer, as listed in AP-42, are as follows:

NO_x	2.7* kg/Mg
SO_x	0.0024
CO	0.068
TSP	0.072
VOC	0.012

1.3.4 Carbon Monoxide Shift

The gas now enters the high and low temperature shift converters, where CO reacts with steam to form CO_2 and H_2. Unreacted steam is condensed and separated from the gas in a knock-out drum. A typical ammonia plant recovers approximately 40 m^3/hr of process condensate for a 900 Mg per day plant.

1.3.5 CO_2 Removal

The gas at this point contains around 17 to 19 percent CO_2 which must be removed since it can poison the ammonia synthesis catalyst. Two scrubbing systems are mainly used in the United States to absorb CO_2: monoethanolamine and hot potassium carbonate. The scrubbing solution is regenerated by heating with steam which generates a 98.5 percent CO_2 stream. Approximately 20 percent of ammonia producers use the carbon dioxide as a chemical feedstock in urea production, thus eliminating the effluent as an air emission. The CO_2 can also be used in tertiary oil recovery. Emission factors are:

Ammonia	1.0 kg/Mg
CO	1.0
VOC	0.48

1.3.6 Methanation

As noted above, CO_2 is a synthesis catalyst poison; therefore, all traces must be removed from the synthesis gas. This is best accomplished by methanation, which is simply a reverse of the catalytic steam reforming of methane.

1.3.7 Emissions From Process Condensate Treatment

Process condensate contains approximately 600 ppm to 1000 ppm ammonia, 200 ppm to 1000 ppm methanol, and 200 ppm to 2800 ppm carbon dioxide. Current practice is for the condensate to be steam stripped and for the

*AP-42 lists 2.9, a misprint.

methanol and ammonia that are removed to be vented to the atmosphere. The stripped condensate is then disposed of. Emission factors for the vented gas are:

Ammonia	1.1 kg/Mg
CO_2	3.4
Methanol	0.6

The least-cost control approach is to inject the overhead from the steam stripper into the reformer furnace stack. At a stack temperature of 200°C to 260°C, ammonia and methanol largely decompose.

1.3.8 Ammonia Synthesis

Synthesis gas is compressed and then fed to the ammonia synthesizer. A small amount of the gas is purged to prevent buildup of inert gas in the reaction cycle. The purge gas is refrigerated to remove ammonia and then fed to the primary reformer along with natural gas. Typical purge gas has the following composition:

Hydrogen	60 mole percent
Nitrogen	20
Argon	3.5
Methane	16.5
Ammonia	50 ppm

1.3.9 Fugitive Emissions

Fugitive emissions arise from leaking compressor and pump seals, ammonia storage tank vents, and pressure relief valves. The ammonia synthesis section of the plant operates at pressures in the range of 3 MPa (400 psi), and leaks are quickly identified and sealed, particularly since the first perceptible odor of ammonia is 20 ppm.

1.3.10 Possible Future Process Improvements

Pullman Kellogg recommends cryogenic recovery of hydrogen from the purge gas. Hydrogen is just too valuable to use as a fuel and, when removed and added to the synthesis gas, recovered hydrogen can increase plant capacity by 6 percent. A membrane separation technique has been developed by Monsanto for the removal of hydrogen from the purge gas. A test unit was installed at Monsanto's 545 Mg/d (600 t/d) ammonia plant in Luling, Louisiana, followed by a commercial unit that started up in September 1979.

Pullman Kellogg has also reportedly succeeded in reducing the synthesis pressure from 14 to 8 kPa which reduces natural gas requirements from 1100 m^3/Mg to 750 m^3/Mg of ammonia produced.

1.4 SUMMARY AND SIGNIFICANCE OF EMISSIONS

Emission factors are summarized in Table 1-1 for both controlled and uncontrolled cases. Also shown in the table are annual emissions from a typical 900 Mg ammonia plant (900 "metric tons" which is about 1000 tons). Finally, the table gives calculated annual emissions for the entire industry based on 1978 NH_3 production of 16.4 Tg. (Annual emissions combine methanol and MEA with VOC as CH_4 equivalent.) Furthermore, uncontrolled emissions assume no controls exist in the existing population, which would tend to over-estimate existing emissions. The controlled situation for the existing population shows that NO_x emissions would increase since reduction of emissions from the CO_2 absorber raises reformer NO_x by 41 percent. The reader should not interpret the difference in emissions between the uncontrolled and controlled existing population as being a possible result of any EPA standard-setting activities since NSS would only apply to new sources. The table also shows the relative contribution of the ammonia industry to the total stationary source emissions.

Table 1-1. SUMMARY OF EMISSIONS

	SO_2	NO_x	CO	TSP	VOC	MeOH	MEA	NH_3
Emission factors, g/Mg NH_3								
Desulfurizer (carbon)	6.0		6,900		3,600			
Controlled (ZnO)	0		0		0			
Reformer	2.4	2,700	68	72	12			
Δ for stripper overhead to stack		+ 1,100				+ 150		+ 440
Steam stripper						600		1,100
Controlled (to reformer stack)						0		0
CO_2 absorber			1,000		470		50	1,000
If feedstock for urea plant			0		0		0	0
Annual emissions: 900 Mg plant, Mg (MeOH and MEA on CH_4 equivalent and included with VOC)								
Uncontrolled	2.5	826	2,438	22	1,346			
Controlled	0.7	1,163	327	22	175			
Controlled, with on-site urea production	0.7	1,163	21	22	27			
National annual emissions (based on 16.4 Tg produced in 1979), Gg								
Uncontrolled	0.14	44.3	130.7	1.2	72.2			
(Percent of all stationary sources)	(0.0005)	(0.34)	(0.75)	(0.01)	(0.42)			
Controlled	0.04	62.3	1.1	1.2	1.2			
(Percent of all stationary sources)	(0.00015)	(0.48)	(0.006)	(0.01)	(0.007)			

2. INTRODUCTION

The United States Congress has mandated that the Environmental Protection Agency promulgate new source performance standards for so-called major source categories; a ranking of 59 such sources was recently published in the Federal Register (44 FR 49222-49226). The standard-setting process involves three principal activities: information gathering, analysis of information, and development of standards. This report comprises the results of the first phase as applied to the synthetic ammonia industry. The report describes the industry, the process, emission sources, and available control technology.

2.1 APPROACH AND ACTIVITIES

The objective of this Source Category Survey Report of the synthetic ammonia industry is to determine the feasibility of setting performance standards for control of air emissions in new sources. Crucial to this task were determinations of growth potential in the industry, location of facilities, production methods and possible process modifications, emission points, quantity of pollutants, and available control technology. To accomplish these tasks several approaches were taken. Authorities in the design, construction, and operation of synthetic ammonia facilities were consulted and several plant site-visits were made. Current status and future prospects of the industry were assessed with the assistance of the Tennessee Valley Authority's National Fertilizer Development Center and The Fertilizer Institute. Air pollution control agencies in states with most of the ammonia facilities were consulted for information on current regulatory controls on the industry. Extensive surveys were made of literature pertaining to production methods and possible emissions from ammonia synthesis. Based on information gathered during these various surveys, judgments were made concerning the future of the industry and the significance of air emissions during the synthesis process.

2.2 THE AMMONIA INDUSTRY

In 1979, there were 101 synthetic ammonia plants reported in the United States, located in 30 states. Of the 101 facilities (a production capacity of 22.5 Tg), 27 are reported idle (a production capacity of 3.5 Tg). In 1979, 16.4 Tg of ammonia was produced.

The industry is not growing and growth is not expected at least through 1985. In addition, a shift to the use of coal gasification to produce a feedstock will not be available in the foreseeable future.

2.3 BACKGROUND AND AUTHORITY FOR STANDARDS

Section 111 of the Clean Air Act as amended (42 USC 7411) directs the Administrator to establish standards of performance for any category of new stationary source of air pollution which ". . . causes, or contributes significantly to air pollution which may reasonably be anticipated to endanger public health or welfare."

The Act requires that standards of performance for stationary sources reflect, ". . . the degree of emission reduction achievable which (taking into consideration the cost of achieving such emission reduction, and any nonair quality health and environmental impact and energy requirements) the Administrator determines has been adequately demonstrated for that category of sources." The standards apply only to stationary sources, the construction or modification of which commences after regulations are proposed by publication in the Federal Register.

The 1977 amendments to the Act altered or added numerous provisions that apply to the process of establishing standards of performance.

1. EPA is required to review the standards of performance every 4 years and, if appropriate, revise them.

2. EPA is authorized to promulgate a standard based on design, equipment, work practice, or operational procedures when a standard based on emission levels is not feasible.

3. The term "standards of performance" is redefined, and a new term "technological system of continuous emission reduction" is defined. The new definitions clarify that the control system must be continuous and may include a low- or non-polluting process or operation.

4. The time between the proposal and promulgation of a standard under Section 111 of the Act may be extended to 6 months.

Standards of performance, by themselves, do not guarantee protection of health or welfare because they are not designed to achieve any specific air quality levels. Rather, they are designed to reflect the degree of emission limitation achievable through application of the best adequately demonstrated technological system of continuous emission reduction, taking into consideration the cost of achieving such emission reduction, any non-air-quality health and environmental impacts, and energy requirements.

Congress had several reasons for including these requirements. First, standards with a degree of uniformity are needed to avoid situations where some states may attract industries by relaxing standards relative to other states. Second, stringent standards enhance the potential for long-term growth. Third, stringent standards may help achieve long-term cost savings by avoiding the need for more expensive retrofitting when pollution ceilings may be reduced in the future. Fourth, certain types of standards for coal-burning sources can adversely affect the coal market by driving up the price of low-sulfur coal or effectively excluding certain coals from the reserve base because their untreated pollution potentials are high. Congress does not intend that new source performance standards contribute to these problems. Fifth, the standard-setting process should create incentives for improved technology.

Promulgation of standards of performance does not prevent state or local agencies from adopting more stringent emission limitations for the same sources. States are free under Section 116 of the Act to establish even more stringent emission limits than those established under Section 111 or those necessary to attain or maintain the National Ambient Air Quality Standards (NAAQS) under Section 110. Thus, new sources may in some cases be subject to limitations more stringent than standards of performance under Section 111, and prospective owners and operators of new sources should be aware of this possibility in planning for such facilities.

A similar situation may arise when a major emitting facility is to be constructed in a geographic area that falls under the prevention of significant deterioration of air quality provisions of Part C of the Act. These provisions require, among other things, that major emitting facilities to be constructed in such areas are to be subject to best available control technology as defined in Section 169(3) of the Act.

2.4 PROCEDURE FOR DEVELOPMENT OF STANDARDS OF PERFORMANCE

Standards of performance must (1) realistically reflect best demonstrated control practice, (2) adequately consider the cost, the non-air-quality health and environmental impacts, and the energy requirements of such control, (3) be applicable to existing sources that are modified or reconstructed as well as new installations, and (4) meet these conditions for all variations of operating conditions being considered anywhere in the country.

The objective of a program for developing standards is to identify the best technological system of continuous emission reduction that has been adequately demonstrated. The standard-setting process involves three principal phases of activity: (1) information gathering, (2) analysis of the information, and (3) development of the standard of performance.

During the information-gathering phase, industries are queried through telephone conversations, letters of inquiry, and plant visits by EPA representatives. Information is also gathered from many other sources, and a literature search is conducted. From the knowledge acquired about the industry, EPA selects certain plants at which emission tests may be conducted to provide reliable data that characterize the pollutant emissions from well-controlled existing facilities.

In the second phase of a project, the information about the industry and the pollutants emitted is used in analytical studies. Hypothetical "model plants" are defined to provide a common basis for analysis. The model plant definitions, national pollutant emission data, and existing state regulations governing emissions from the source category are then used in establishing "regulatory alternatives." These regulatory alternatives are essentially different levels of emission control.

EPA conducts studies to determine the impact of each regulatory alternative on the economics of the industry and on the national economy, on the environment, and on energy consumption. From several possibly applicable alternatives, EPA selects the single most plausible regulatory alternative as the basis for a standard of performance for the source category under study.

In the third phase of a project, the selected regulatory alternative is translated into a standard of performance, which, in turn, is written in the

form of a Federal regulation. The Federal regulation, when applied to newly constructed plants, will limit emissions to the levels indicated in the selected regulatory alternative.

2.5 REVISION OF STANDARDS OF PERFORMANCE

Congress was aware that the level of air pollution control achievable by any industry may improve with technological advances. Accordingly, Section 111 of the Act provides that the Administrator ". . . shall, at least every 4 years, review and, if appropriate, revise . . ." the standards. Revisions are made to assure that the standards continue to reflect the best systems that become available in the future. Such revisions will not be retroactive, but will apply to stationary sources constructed or modified after the proposal of the revised standards.

2.6 CURRENT STATE REGULATIONS RELATIVE TO THE AMMONIA INDUSTRY

Air pollution control agencies of the five states with the largest number of ammonia plants were contacted for information on state regulatory stance toward synthetic ammonia plants. All contacts indicated that their respective states had no specific regulations regarding emissions from the ammonia synthesis (Spuhler, 1980; Brasher, 1980; Wall, 1980; Argentine, 1980; Cullen, 1980). No control technology for air emissions from existing facilities is currently required by any of these states. State agencies indicated that permit requests for new sources would be handled on a case by case basis. Items of concern would include the impact of the source on National Ambient Air Quality Standards (NAAQS) as outlined in the State Implementation Plans (SIP). Where necessary, emissions would be controlled by best control technology available within economic constraints.

3. CONCLUSIONS

3.1 CONCLUSIONS

3.1.1 Growth

The domestic ammonia manufacturing industry is entering a sustained period of no growth in production capacity. While there will be an increase in demand for ammonia, particularly in the form of nitrogen fertilizers, the domestic industry has sufficient excess capacity to meet demands at least through 1985.

3.1.2 Significant Emission Sources/Control Technology

A typical nominal size 900 Mg per day ammonia plant will have the following annual emissions:

Species	Mg/Year	Source
NO_x	1163	Reformer
CO	327	Reformer and CO_2 Absorber
VOC	175	Reformer and CO_2 Absorber

These emissions assume that natural gas is desulfurized with zinc oxide and that condensate steam stripper overhead is fed to the reformer stack. If the CO_2-rich stream from the CO_2 sorbent regeneration is used for urea production or tertiary oil recovery, CO and VOC are reduced to 21 Mg and 27 Mg per year, respectively. Historically, plants have employed activated carbon to desulfurize the natural gas. The carbon is regenerated with steam which, when vented to the atmosphere, increases the plant's CO and VOC emissions to 2438 Mg and 1346 Mg per year, respectively. The recent trend and future approach is to use zinc oxide which is disposed of as a solid rather than being regenerated. In addition to removing this emission point, steam requirements are eliminated. Also, carbon adsorbs higher molecular weight hydrocarbons, thus reducing the heating value of the gas.

4. THE AMMONIA MANUFACTURING INDUSTRY

4.1 POPULATION

In 1979 a total of 101 synthetic ammonia plants with a rated production capacity of 22.5 Tg (24.8×10^6 tons) per year were reported in 30 states. Production in 1979 was 16.4 Tg (18×10^6 tons), or 73 percent of capacity. Twenty-seven plants were reported idle in March 1980, representing 3.5 Tg (3.9×10^6 tons). Currently, the heaviest concentration of production in the United States is in the natural-gas producing states of Texas and Louisiana which contain 17 and 15 sites, respectively. The five states of Texas, Louisiana, California, Iowa, and Oklahoma contain 70 percent of the total production capacity.

Appendix A contains a list of United States ammonia plants, their location, nameplate production capacity, and status as furnished by TVA (Harre, 1980). A state-by-state listing of plant locations is included.

4.2 INDUSTRY PRODUCTION

Domestic production of anhydrous ammonia has followed a pattern of decelerating growth during the 1970's following rapid growth during the 1960's. As shown in Figure 4-1, increase in production during the early 1960's approximated an exponential rate. During the 1970's the growth rate slowed to an average increase of 2.9 percent per year. As shown in Table 4-1, production of ammonia in 1970 was 12.6 teragrams (14.0×10^6 tons) as NH_3. In 1979, the figure was 16.4 Tg (18.0×10^6 tons).

This steady increase in production masks the highly variable market conditions for ammonia during the same period. As shown in Table 4-2 and Figure 4-2, the actual consumption of nitrogen fertilizers varied as much as 10 percent from year to year in the 1970's. Since fertilizer accounts for the largest single use of ammonia in the United States, agricultural demand patterns have a great impact on the industry.

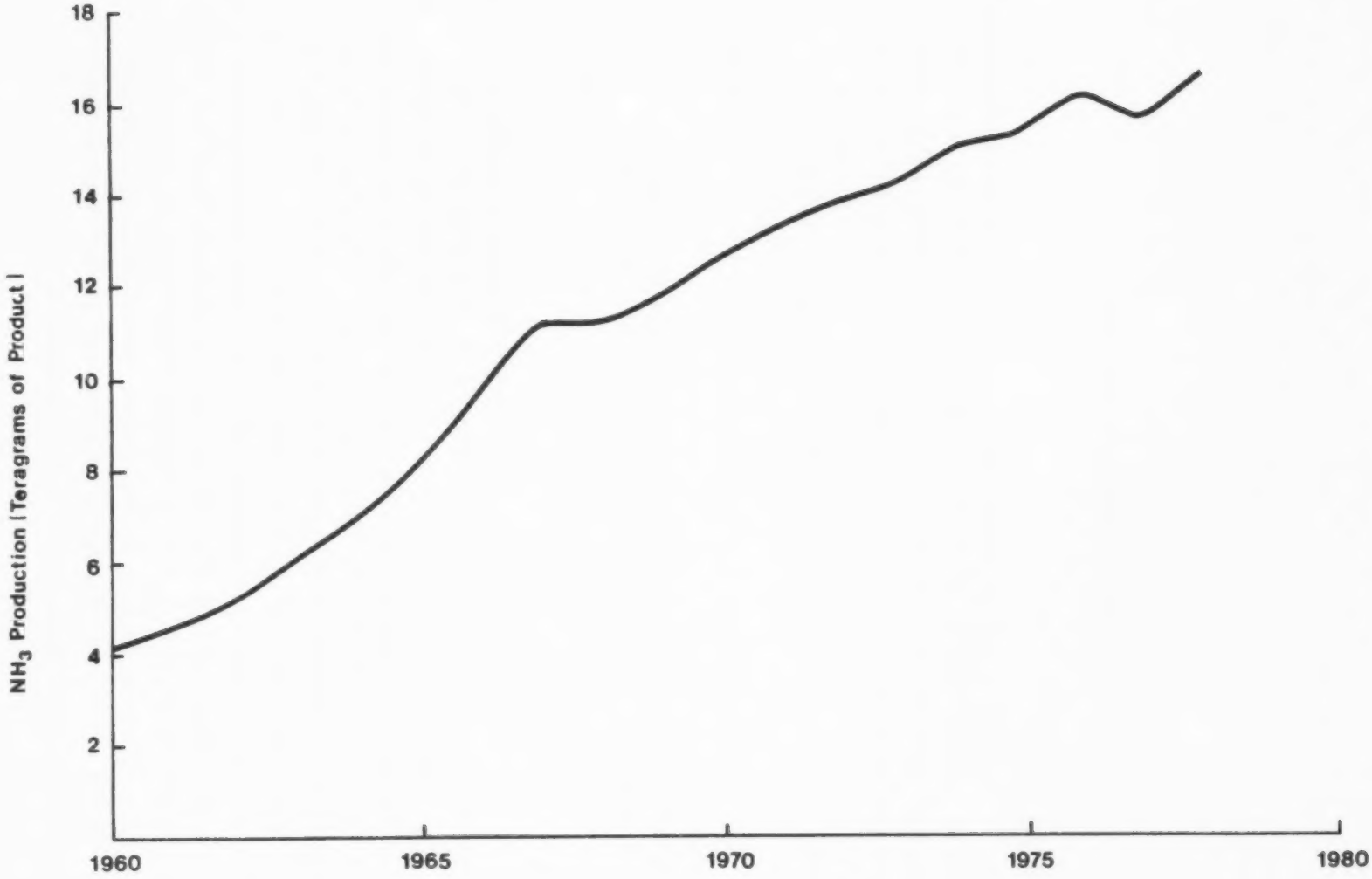

Figure 4-1. Annual United States production of ammonia.

Table 4-1. UNITED STATES PRODUCTION OF ANHYDROUS AMMONIA[a]

Year	Annual production Tg (10^6 short tons) as NH_3	
1970	12.56	(13.82)
1971	13.22	(14.54)
1972	13.74	(15.17)
1973	13.82	(15.21)
1974	14.30	(15.73)
1975	14.92	(16.42)
1976	15.19	(16.72)
1977	15.98	(17.57)
1978	15.40	(16.95)
1979	16.40	(18.00)

[a]Bridges, 1979 and U. S. Department of Commerce, 1979.

Table 4-2. UNITED STATES CONSUMPTION OF NITROGEN FERTILIZERS[a]

Year	Annual consumption Tg (10^6 short tons) as NH_3	
1970	8.27	(9.10)
1971	9.02	(9.91)
1972	8.89	(9.78)
1973	9.20	(10.12)
1974	10.15	(11.16)
1975	9.53	(10.49)
1976	11.54	(12.68)
1977	11.80	(12.98)
1978	11.04	(12.14)
1979	11.80	(12.98)

[a]Bridges, 1979.

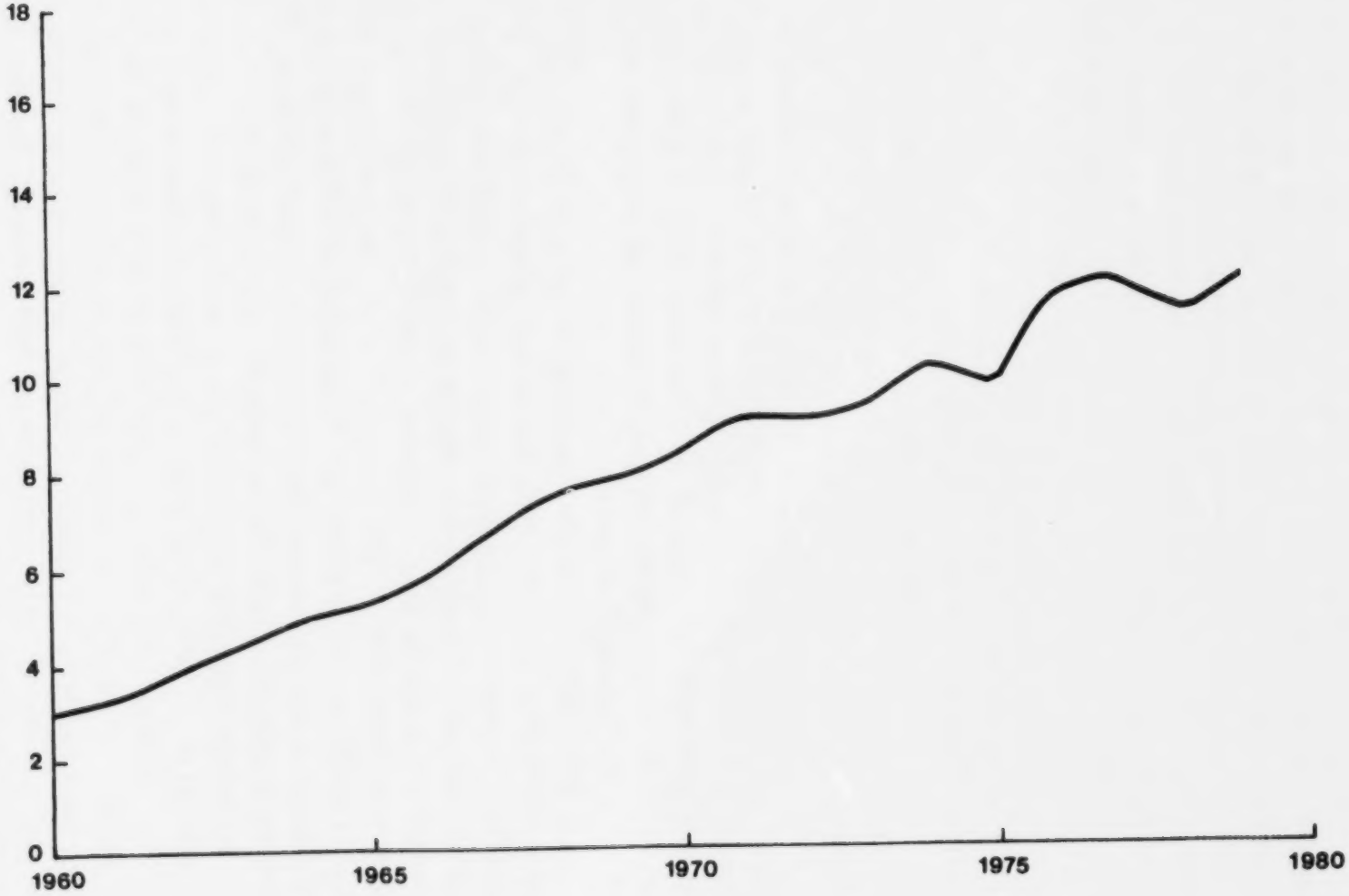

Figure 4-2. Nitrogen fertilizer consumption

Prices for anhydrous ammonia have fluctuated widely in response to demand. In 1975, ammonia was in short supply worldwide and prices ranged from $220 to $440 per megagram ($200 to $400 per ton) (Wett, 1979). To meet the demand the industry increased production capacity by about 20 percent or 14 Tg (15 million tons) per year worldwide (Wett, 1979). Faced with an eventual abundance in supplies and a lessening in demand, ammonia prices plummeted to less than $100 per ton in 1978 (United States Department of Agriculture, 1979; Wett, 1979). The price squeeze has caused the closure or delayed start-up of many facilities. Over 3.5 Tg (3.9×10^6 tons) of the 22.5 Tg (24.8×10^6 tons) of United States capacity was reported closed as of February 28, 1980 (Johnson, 1980a).

The future of the synthetic ammonia industry in the United States will be determined by such factors as import competition and regulation, fertilizer demand, and natural gas price and availability.

Currently, over 95 percent of the ammonia produced in the United States uses natural gas as a feedstock. The cost of natural gas is a significant factor in the production cost of ammonia. Table 4-3 shows the ammonia production cost based on data from Wett (1979) as provided by M. W. Kellogg. At $2/GJ ($2/MBtu) the cost of natural gas represents over half of the production costs of ammonia.

At this point, predictions concerning the price of natural gas in 5 years are highly tentative. With the eventual deregulation of gas prices, price will be more closely tied to market forces of supply and demand. As the current gas contracts expire, any new contracts will be written with flexible price arrangements. Estimates of the 1985 price of natural gas have ranged from $3/GJ in 1978 dollars to $6/GJ. The lower price, which was the worst-case price projection in the Energy Information Administration's 1978 Annual Report to Congress (United States Department of Energy, 1978), is already outdated. Under the incremental pricing system imposed by the Federal Energy Regulatory Commission, the price of industrial natural gas in some states is currently as high as $3.80/GJ. As shown above, the increase in natural gas price will have a significant effect on the price of ammonia. If the price of natural gas rose to $6/GJ while holding all other costs constant, the production cost of ammonia would be $260/Mg ($240 per ton). Of course, other costs have not held constant. The cost of a new ammonia plant has doubled since 1978 to 120 million dollars (Scholer, 1980).

Table 4-3. AMMONIA PRODUCTION COSTS[a]

Raw material	Unit cost	Unit rate	$/day
Natural gas feed	$2/GJ	1053 GJ/hr	50,544
Utilities			
Fuel	$2/GJ	534 GJ/hr	25,632
Power	2¢/kWh	70 kW	355
Cooling water make-up	6.6¢/m^3	5.6 m^3/min	532
Boiler feed water make-up	26.4¢/m^3	1.7 m^3/min	646
Steam		In balance	-
Other			
Catalyst and chemicals		$1.60/Mg	1,672
Labor		5 men/shift, $6/man-hr	720
Labor and plant overhead		100% labor	720
Indirect charges and pre-tax return on investment		35% of investment	61,765
Total cost			142,586 ($136.45/Mg)

[a]Basis: 1045 Mg/day
Capital investment $60 million
Includes cooling tower, boiler feed water treating, and nominal product storage
Excludes spare parts
Indirect charges: 10% depreciation, 3.5% maintenance, 1.5% taxes and insurance, 20% return on investment (pretax)

The availability of natural gas at any price is increasingly crucial to the ammonia industry. The Powerplant and Industrial Fuel Use Act of 1978 and the subsequent regulations issued by the Department of Energy are designed to restrict industrial use of oil and natural gas. Accordingly, the use of natural gas and oil in boilers built after 1978 is prohibited subject to provisions of technical and economic feasibility.

Most natural gas is supplied to industry on an interruptible basis. Winter curtailment of natural gas supplies has had a definite impact on the industry. Natural gas curtailments in fertilizer year 1977 (from July 1976 to June 1977) were said to represent a 680 Gg (760 x 10^3 tons) loss in ammonia production that year (The Fertilizer Institute, 1979).

In anticipation of increasing curtailment of natural gas supplies, several projects have investigated the feasibility of using coal as a fuel and a source of gas feedstock for the production of ammonia. A TVA ammonia production facility is being retrofitted to use coal gas as both a feedstock and a fuel. This facility is tentatively scheduled for start-up in August 1980, and will be used as an experimental system to investigate a variety of operating conditions and feedstock mixtures (Waitzman et al., 1978).

A second, larger project investigating the feasibility of using coal gas in ammonia production was initiated as a joint venture between W. R. Grace, Inc., and the Energy Research and Development Administration (Savage, 1977). As originally planned, a demonstration plant would synthesize gas from coal using the Texaco process. This gas would then be sold to W. R. Grace for use in ammonia synthesis. After the design phase of this project, funding was terminated by the Department of Energy in favor of a project to convert coal to intermediate Btu gas for industrial use (Stewart, 1980). Given the experimental nature of "ammonia from coal" technology and the cost of retooling the industry, it is unlikely that a significant shift in production methods will occur in the next 5 to 10 years.

The major effect of natural gas availability and cost on ammonia production will be on the siting of new production facilities. Several developing countries with new-found oil and gas supplies have recently begun to expand ammonia production capabilities. Conversion of natural gas to ammonia provides a convenient use for excess gas supply that might

otherwise be flared. Countries with this production potential include Mexico and Trinidad as well as some of the older OPEC nations (The Fertilizer Institute, 1979). Shields and McIntyre (1979) predict that one-fourth of the world's fertilizer will be produced in developing countries by 1985 compared with 10 percent in 1969. Whether these new producers have disruptive effect on the market will depend on trade agreements and orderly market arrangements.

The current trade embargo with USSR could have a significant effect on the ammonia market in both a direct and indirect fashion. Predictions made in 1979 indicated that almost 10 percent of current United States demand for ammonia would be supplied by imports from Russia by 1980 (Wett, 1979). Current predictions from the United States Department of Agriculture are that ammonia imports from Russia will be between 0.7 and 0.9 Tg in 1981 (Maxey, 1980). Curtailment of this source could result in a new demand for domestic supplies. On the other hand, the grain embargo could soften the market for agricultural products with a subsequent reduction in demand for fertilizer. In the short term then, the ammonia market appears certain to follow a pattern of volatility and unpredictability.

Despite the short-term uncertainties, several conclusions can be drawn on the direction of the industry for the next 5 years. Demand for nitrogen fertilizers will continue to show steady growth spurred by the increasing need for agricultural products. Increased agricultural production will require the use of marginally productive lands which have a proportionally higher fertilizer requirement. The domestic demand for nitrogen fertilizer is predicted to increase from 1978 levels of 14.3 Tg (15.8 million tons) as NH_3 to 17.4 Tg (19.1 million tons) in 1985 (Shields and McIntyre, 1979). Worldwide demand is expected to climb from 58.0 Tg (63.8 million tons) to 80.1 Tg (88.2 million tons) in the same period (Shields and McIntyre, 1979). Douglas (1978) predicts a 3 percent annual growth rate in nitrogen fertilizer consumption through 1990 in the United States.

Ammonia prices have recovered from levels of around $100/Mg ($90/ton) to a more profitable level of $160/Mg ($145/ton) as of December 1979 (United States Department of Agriculture, 1979). With the increase in ammonia prices, several idle plants may come back on line; however, any new plant

expansion is unlikely. Both domestic and worldwide production capabilities are sufficient to handle predicted demand through 1985 (Bridges, 1979). The most recent semi-annual survey of the ammonia industry conducted by The Fertilizer Institute indicates that no domestic plants are planned for construction through 1984 (Johnson, 1980b). Beyond that period it is likely that the increased cost of feedstock will force nitrogen production to shift from traditional producers such as the United States, Japan, and Western Europe to areas of available low-cost natural gas (Shields and McIntyre, 1979).

The forms in which nitrogen fertilizer is marketed and used have been changing. Consumption of urea is increasing fairly rapidly (10-20 percent per year) while production of ammonium nitrate has leveled off. Urea is favored because of its higher nitrogen content and production methods that avoid the environmental problems associated with the use of nitric acid in the production of ammonium nitrate. While urea production capability may be retrofitted to existing ammonia plants, the increased demand for urea is not sufficient to require new construction of ammonia plants.

Given the current and projected energy supply picture and the relatively unprotected status of the industry, the long-term prognosis for the United States ammonia industry would not appear favorable; however, there is substantial pressure by industry groups to prevent a significant deterioration of this production capacity. This position was made apparent by all parties consulted during this study. Without protection from inexpensive imports the domestic industry could well be submerged by a flood of imports. Protectionist arguments can be based on national security. Because ammonia supply is fundamental to agricultural production, it would not be in the national interest to be held captive by an ammonia cartel.

Despite this protectionist sentiment, it is unlikely that the United States ammonia industry will see any expansion through 1985. The idle and reserve capacity are sufficient to handle the demand for several years. The uncertainties in market conditions, import competition, and raw material supply all weigh against domestic industry growth.

4.3 PROCESS DESCRIPTION

Ninety-eight percent of the ammonia produced in the United States is by catalytic steam reforming of natural gas (Hincman and Spawn, 1979). The gas is converted to hydrogen, purified, and reacted with nitrogen to produce ammonia. In consideration of the increasing cost and decreasing availability of natural gas, many have contemplated gasifying coal to produce synthesis gas. This approach would double the cost of an ammonia plant (Waitzman et al., 1978), and would increase energy consumption by 30 percent and necessitate coal handling and preparation as well as ash disposal (Nichols and Blouin, 1979). Accordingly, the discussion that follows is based on the synthesis of ammonia using natural gas as a feedstock. Appendix B contains a brief discussion of the development of the ammonia synthesis process.

4.3.1 Overall Process

Figure 4-3 is a generalized flow diagram of a typical ammonia plant. The production of ammonia from natural gas comprises six major steps:

1. Desulfurization (to prevent poisoning the nickel reformer catalyst)
2. Reforming of CH_4 to H_2 and CO
3. Shifting of CO with H_2O to produce additional H_2
4. Absorption of CO_2
5. Methanation of residual CO_2 prior to NH_3 synthesis
6. Synthesis of NH_3 from H_2 and N_2

4.3.2 Desulfurization

Natural gas is delivered to the plant at above 3.5 MPa (500 psi) (Mayes, 1980). Natural gas contains sulfur in the form of H_2S which must be reduced to below 280 $\mu g/m^3$ (Rawlings and Reznik, 1977) to prevent poisoning the nickel reforming catalyst (LeBlanc et al., 1978). There are two common desulfurization methods: activated carbon and zinc oxide. With activated carbon two tanks are commonly used so that when one is being regenerated the other is on stream. Regeneration is accomplished by passing superheated steam through the bed. Newer plants are tending to use a zinc oxide bed which remains in the gas stream until it has adsorbed about 20 percent of its weight in sulfur at which time it is discarded (LeBlanc, 1978). There are basicially three advantages to the zinc oxide bed: energy in the form of steam regeneration is not required, there are no air emissions, and

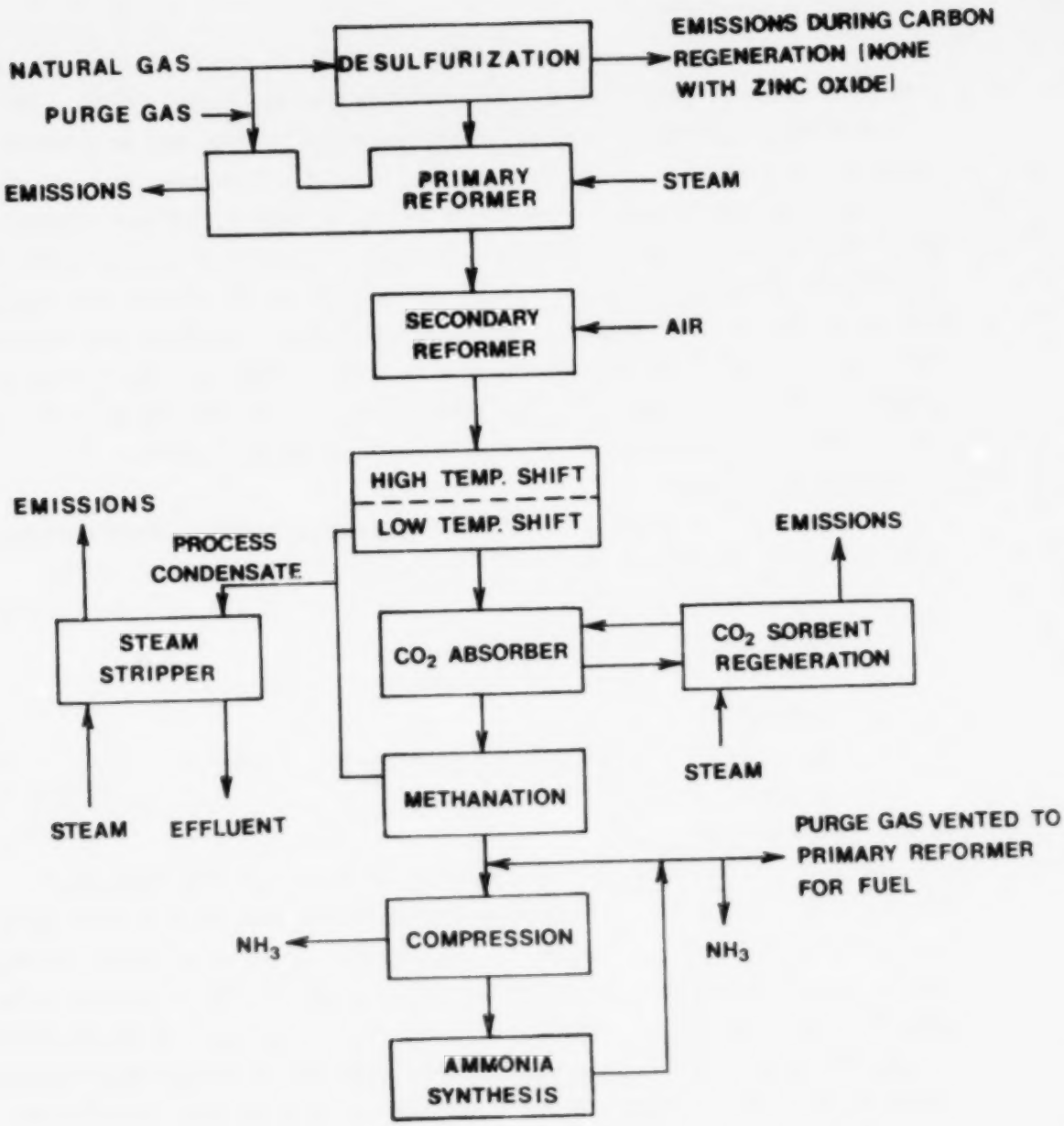

Figure 4-3. Process flow diagram of a typical ammonia plant.

higher molecular weight hydrocarbons are not removed, (which would reduce the heating value of the gas). According to Finneran et al. (1972), heavy hydrocarbons tend to nullify the effectiveness of the carbon. Also, carbon does not remove carbonyl sulfide.

According to CF Industries (Carville, 1980) and Triad Chemicals (Crochet and Torres, 1980) regeneration of the carbon bed occurs once a week and takes twelve hours. Rawlings and Reznek (1977) on the other hand report that regeneration occurs monthly and takes ten hours.

4.3.3 Catalytic Steam Reforming

Steam reforming proceeds in two steps. In the primary reformer (the radiant section of the reformer), methane reacts with steam in the presence of a nickel catalyst to produce hydrogen and CO_2 as follows:

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

$$CO + H_2O \rightarrow CO_2 + H_2$$

Gas exits the primary reformer at 750 to 850°C and 2900 to 3600 kPa (LeBlanc et al. 1978), and contains about 10 percent unreacted methane (Mayes, 1980).

Partially reformed gas flows to the refractory-lined secondary reformer where it is mixed with air (the amount of which is fixed by the ultimately-required H_2/N_2 ratio of 3 to 1). Fuel for the primary reformer consists of 7/8 natural gas and 1/8 purge gas from the ammonia synthesizer (Mayes, 1980). The oxygen from the air is combusted with the fuel to provide additional heat in the secondary reformer. Reformed synthesis gas leaves the secondary reformer at around 1000°C and is cooled to around 370°C, which produces sufficient heat to supply from 50 to 100 percent of the 10.3 MPa steam required in the plant (Rawlings and Reznik, 1977). Methane content at this point is 0.34 percent (Mayes, 1980).

4.3.4 Carbon Monoxide Shift

The gas now enters the high temperature shift converter, which is filled with chromium-oxide-promoted iron oxide shift catalyst (Rawlings and Reznik, 1977) where the shift reaction occurs.

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

The forward reaction proceeds more rapidly at higher temperatures; however, the forward reaction is only partially completed under these conditions. Most of the reaction takes place at high temperature (330 to 550°C) to take advantage of higher rates. At the point that CO_2 builds up to where the reverse reaction can proceed at an appreciable rate, the gas is fed to the low temperature shift reactor (200°C) to take advantage of higher equilibrium CO_2/H_2 concentrations. The CO concentration is reduced from 12.8 percent to 3 percent in the high temperature shift reactor and from 3 percent to 0.5 percent in the low temperature shift reactor. Unreacted steam is condensed and separated from the gas in a knock-out drum. A typical ammonia plant recovers approximately 40 m^3/hr of process condensate for a 900 Mg per day plant.

4.3.5 CO_2 Removal

The gas at this point contains around 17 to 19 percent CO_2 which must be removed since it can poison the ammonia synthesis catalyst. Two scrubbing systems are mainly used in the United States to absorb CO_2: monoethanolamine and hot potassium carbonate (Rawlings and Reznik, 1977). CO_2 is absorbed by monoethanolamine as follows:

$$2NH_2\text{-}C_2H_4\text{-}OH + CO_2 \rightarrow (NH_2\text{-}C_2H_4)_2CO_3 + H_2O$$

and by potassium carbonate solution as follows:

$$CO_3^{=} + CO_2 + H_2O \rightarrow 2HCO_3^{-}$$

The scrubbing solution is regenerated by heating with steam which generates a 98.5 percent CO_2 stream.

4.3.6 Methanation

As noted above, CO_2 is a synthesis catalyst poison; therefore, all traces must be removed from the synthesis gas. This is best accomplished by methanation, which is simply a reverse of the catalytic steam reforming of methane. Specifically, the synthesis gas passes over a nickel catalyst where the following reactions take place:

$$CO_2 + H_2 \rightarrow CO + H_2O$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

Exit gas from the methanator contains less than 10 ppm CO and CO_2 and about 1.3 percent methane and argon. The H_2 to N_2 ratio is 3 to 1.

4.3.7 Ammonia Synthesis

Synthesis gas is compressed in two steps. After the first step, water is removed and the gas is cooled to increase volumetric efficiency. Also, the synthesis gas is combined with recycle from the ammonia synthesizer. Recycle contains 12 percent NH_3 which is reduced to 9.9 percent when mixed with fresh feed. Following final compression, the gas is cooled to $-23^{o}C$ and the ammonia product is removed as is water plus any residual CO/CO_2. Synthesis gas is reheated to $140^{o}C$. It is then fed to the ammonia synthesizer which operates around 14 kPa. The gas exiting the reactor is recycled as described above. A small amount of the gas is purged to prevent buildup of inert gas in the reaction cycle. The purge gas is refrigerated to remove ammonia and then fed to the primary reformer along with natural gas (Rawlings and Reznik, 1977; LeBlanc et al., 1978; Quartulli et al., 1977; Mayes, 1980). Haslam and Isalski (1975) reported that typical purge gas has the following composition:

Hydrogen	60 mole percent
Nitrogen	20
Argon	3.5
Methane	16.5
Ammonia	50 ppm

4.3.8 Possible Future Process Improvements

Pullman Kellogg recommends cryogenic recovery of hydrogen from the purge gas (Ricci, 1979). Hydrogen is just too valuable to use as a fuel and when removed and added to the synthesis gas, recovered hydrogen can increase plant capacity by 6 percent (Ricci, 1979). MacLean et al. (1980) recently reported on a membrane separation technique developed by Monsanto for the removal of hydrogen from the purge gas. A test unit was installed at Monsanto's 545 Mg/d (600 t/d) ammonia plant in Luling, Louisiana, followed by a commercial unit that started up in September 1979.

Pullman Kellogg has also reportedly succeeded in reducing the synthesis pressure from 14 to 8 kPa which reduces natural gas requirements from 1100 m^3/Mg to 750 m^3/Mg of ammonia (Savage, 1977).

5. AIR EMISSIONS

5.1 DESULFURIZATION

Sulfur content in natural gas comprises a broad range; however, gas in the southeast where the majority of NH_3 is synthesized is in the range of 300 to 400 $\mu g/m^3$ (as H_2S). United States Environmental Protection Agency (1979) gives a typical national H_2S content of 4600 $\mu g/m^3$, which will be used in this analysis. Based on a feedstock natural gas requirement of 700 m^3/Mg NH_3, the emission factor for SO_2 is 6 g/Mg NH_3. Furthermore 4600 $\mu g/m^3$ corresponds to approximately 1.2×10^{-4} g sulfur per MJ (3×10^{-4} lb/10^6 Btu) which is four orders of magnitude less than Federal emission standard for the combustion of fossil fuels. Emission factors for SO_2, CO, and VOC are 6 g/Mg, 6.9 kg/Mg and 3.6 kg/Mg, respectively (Rawlings and Reznek, 1977). Based on a 900 Mg per day ammonia plant, annual emissions for SO_2, CO, and VOC are 1.8 Mg, 2100 Mg, and 1100 Mg, respectively. According to Hincman and Spawn (1979), a few producers have installed incinerators, despite the added cost, to combust the CO and VOC. Industry consensus is that new ammonia plants will use zinc oxide rather than carbon which would eliminate the desulfurizer as an emission point (Finneran et al., 1972; Carville, 1980; Crochet and Torres, 1980; and Lukes et al., 1980). According to Buividas (1980), it is more cost effective to use zinc oxide where sulfur content is below 10 ppm (12 mg/m^3).

5.2 CATALYTIC STEAM REFORMING

Emission factors for the primary reformer were calculated by Rawlings and Reznik (1977) for both natural gas and No. 2 fuel oil based upon lab tests and reported emissions at four ammonia plants. These emission factors, which are those listed in AP-42, are as follows:

Species	Natural Gas, kg/Mg	Fuel Oil, kg/Mg
NO_x	2.7*	2.7
SO_x	0.0024	1.3
CO	0.068	0.12
TSP	0.072	0.45
VOC	0.012	0.15

5.3 REGENERATION OF CO_2 SORBENT

The scrubbing solution is regenerated by heating with steam which generates a 98.5 percent CO_2 stream. Approximately 20 percent of ammonia producers use the carbon dioxide as a chemical feedstock in urea production thus eliminating the effluent as an air emission (Hincman and Spawn, 1979). Emission factors, which are based on the work of Rawlings and Reznik (1977), are listed in AP-42 as follows:

CO	1.0
VOC	0.48

5.4 EMISSIONS FROM PROCESS CONDENSATE TREATMENT

Most of the process condensate arises from the low temperature shift where unreacted steam is condensed and separated from the gas in a knock-out drum. This water contains approximately 600 ppm to 1000 ppm ammonia, 200 ppm to 1000 ppm methanol, and 200 ppm to 2800 ppm carbon dioxide (Romero et al., 1977). Additional condensate is removed from the cooled gas that leaves the methanator. Current practice is for the condensate to be steam stripped and for the methanol and ammonia that are removed to be vented to the atmosphere. The stripped condensate is then disposed of (Rawlings and Reznik, 1977). At least one plant uses the unstripped condensate directly as feed to a low-pressure boiler (Lukes et al., 1980). Emission factors for the vented gas are listed in AP-42 as follows:

Ammonia	1.1 kg/Mg
CO_2	3.4
Methanol	0.6

*AP-42 lists 2.9, a misprint.

According to Romero et al. (1977) the least-cost and most acceptable control approach is to inject the overhead from the steam stripper into the reformer furnace stack. At a stack temperature of 200°C to 260°C, ammonia and methanol largely decompose. Actual stack analysis showed that ammonia and methanol were reduced by 59.3 and 74.7 percent, respectively. This may not be a particularly efficacious control technique since the result of NH_3 decomposition is a 41 percent increase in NO_x (Rawlings and Reznik, 1977).

5.5 FUGITIVE EMISSIONS

As noted above, fugitive emissions arise form leaking compressor and pump seals, ammonia storage tank vents, and pressure relief valves. The ammonia synthesis sections of the plant operates at pressures in the range of 3 MPa (400 psi), and leaks are quickly identified and sealed, particularly since the first perceptible odor of ammonia is 20 ppm (LeBlanc et al., 1978). One plant (Crochet and Torres, 1980) reported NO_x emissions while flaring ammonia from the storage tank. They reported 2 tons of ammonia flared per day for about 15 days per year. Most plants, however, use a small compressor to recompress NH_3 off-gas from the storage tank when the plant is down (Johnson, 1980c).

5.6 SUMMARY AND SIGNIFICANCE OF EMISSIONS

Emission factors are summarized in Table 5-1 for both controlled and uncontrolled cases. Also shown in the table are annual emissions from a typical 900 Mg ammonia plant (900 "metric tons" which is about 1000 tons). Finally, the table gives calculated annual emissions for the entire industry based on 1978 NH_3 production of 16.4 Tg. Annual emissions combine methanol and MEA with VOC as CH_4 equivalent. Furthermore, uncontrolled emissions assume no controls exist in the existing population, which would tend to over-estimate existing emissions. The controlled situation for the existing population shows that NO_x emissions would increase since reduction of emissions from the CO_2 absorber raises reformer NO_x by 41 percent. The reader should not interpret the difference in emissions between the uncontrolled and controlled existing population as being a possible result of any EPA standard-setting activities since NSS would only apply to new sources. The table also shows the relative contribution of the ammonia industry to the total stationary source emissions.

Table 5-1. SUMMARY OF EMISSIONS

	SO_2	NO_x	CO	TSP	VOC	MeOH	MEA	NH_3
Emission factors, g/Mg NH_3								
Desulfurizer (carbon)	6.0		6,900		3,600			
Controlled (ZnO)	0		0		0			
Reformer	2.4	2,700	68	72	12			
Δ for stripper overhead to stack		+ 1,100				+ 150		+ 440
Steam stripper						600		1,100
Controlled (to reformer stack)						0		0
CO_2 absorber			1,000		470		50	1,000
If feedstock for urea plant			0		0		0	0
Annual emissions: 900 Mg plant, Mg (MeOH and MEA on CH_4 equivalent and included with VOC)								
Uncontrolled	2.5	826	2,438	22	1,346			
Controlled	0.7	1,163	327	22	175			
Controlled, with on-site urea production	0.7	1,163	21	22	27			
National annual emissions (based on 16.4 Tg produced in 1979), Gg								
Uncontrolled	0.14	44.3	130.7	1.2	72.2			
(Percent of all stationary sources)	(0.0005)	(0.34)	(0.75)	(0.01)	(0.42)			
Controlled	0.04	62.3	1.1	1.2	1.2			
(Percent of all stationary sources)	(0.00015)	(0.48)	(0.006)	(0.01)	(0.007)			

6. EMISSION CONTROL

6.1 DESULFURIZATION

As noted in Chapter 5, activated carbon will not be used in future plants to desulfurize the natural gas feedstock. Since the zinc oxide is not regenerated, there are no air emissions from this step in the process.

6.2 REFORMER

Process heat for the primary reformer is supplied by burning natural gas or, in a few isolated instances, fuel oil. Emissions are the combustion products, mainly NO_x, which can be reduced by combustion modification or ammonia injection into the combustion zone.

6.3 CO_2 SORBENT REGENERATION

The 98 percent CO_2 gas stream is commonly vented to the atmosphere. Since the gas contains CO and VOC (which corresponds to annual emissions of 306 Mg and 148 Mg, respectively, for a 900 Mg per day ammonia plant), an alternative is desirable. It was noted that approximately 20 percent of the ammonia producers use the CO_2 stream in urea production. Since there is significant growth in urea production, existing ammonia plants are being retrofitted with urea plants. It may be reasonably expected that any new ammonia plants constructed beyond 1985 will be in conjunction with urea production, thus eliminating the CO_2 stream as an emission point in the process.

6.4 PROCESS CONDENSATE STRIPPING

Methanol contained in the overhead gas from the condensate stripper results in an annual VOC emission of about 92 Mg from a 900 Mg per day ammonia plant. This is reduced to about 23 Mg per year when the gas stream is injected to the base of the reformer stack.

6.5 CONTROL OF FUGITIVE EMISSIONS

As was noted in Chapter 5, the ammonia synthesis section of the plant operates at high pressure such that any leaks are quickly identified and sealed, particularly since ammonia is the product which the owner does not wish to lose.

7. EMISSION DATA

This study is based on emissions reported in a 1977 EPA survey report on the ammonia manufacturing industry (Rawlings and Reznik, 1977). In addition, process condensate treatment at seven ammonia plants was examined in 1977 and was published in an EPA report (Romero et al., 1977). No source testing was performed under the current study. Indeed, the plants that were visited during this study base their emission estimates on AP-42 (USEPA, 1979). There is no evidence that any independent emission data exist in the industry.

8. STATE AND LOCAL EMISSION REGULATIONS

Air pollution control agencies of the five states with the largest number of ammonia plants were contacted for information on state regulatory stance toward synthetic ammonia plants. All contacts indicated that their respective states had no specific regulations regarding emissions from the ammonia synthesis (Spuhler, 1980; Brasher, 1980; Wall, 1980; Argentine, 1980; Cullen, 1980). No control technology for air emissions from existing ammonia manufacturing facilities is currently required by any of these states. State agencies indicated that permit requests for new sources would be handled on a case by case basis. Items of concern would include the impact of the source on National Ambient Air Quality Standards (NAAQS) as outlined in the State Implementation Plans (SIP). Where necessary, emissions would be controlled by best control technology available within economic constraints.

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APPENDIX A. INDUSTRY DESCRIPTION

Table A-1 is a list of ammonia plants, location, capacity, and status (Harre, 1980; Blue, 1980). The designation "closed" indicates that the facility has been shut down with little prospect for reopening. The designation "idle" indicates that the plant has been shut down in a non-routine fashion but may be brought back up if conditions improve. The date following the designation indicates the year in which the plant was shut down. Production data are presented as daily production capacity. Annual production capacity is typically figured by assuming 340 production days per year.

Table A-2 lists all ammonia plants that were shut down as of March 1980 (Johnson, 1980a). Table A-3 provides a distribution of ammonia plants by state.

Table A-1. U. S. AMMONIA PLANTS AND CAPACITIES (1980 YEAR-END)

Company, location	Status	Daily capacity Mg* (tons) as NH_3
Agrico		
Blytheville, Arkansas	Operational	1,090 (1,200)
Donaldsonville, Louisiana	Operational	1,250 (1,375)
Verdigris, Oklahoma	Operational	2,250 (2,500)
Air Products		
Pace, Florida	Operational	250 (290)
New Orleans, Louisiana	Operational	560 (610)
Allied		
Helena, Arkansas	Operational	560 (610)
Geismar, Louisiana	Operational	900 (1,000)
Omaha, Nebraska	Operational	460 (500)
South Point, Ohio	Closed (1978)	530 (580)
Hopewell, Virginia	Operational	910 (1,000)
American Cyanamid		
Avondale, Louisiana	Operational	820 (2,000)
Amoco		
Texas City, Texas	Operational	1,400 (1,500)
Texas City, Texas	Idle (1977)	540 (600)
Ampro (First Mississippi Corp.)		
Donaldsonville, Louisiana	Operational	1,070 (1,176)
Apache Powder		
Curtiss, Arizona	Idle (1979)	34 (38)

(continued)

Table A-1. (Continued)

Company, location	Status	Daily capacity Mg* (tons) as NH_3
Atlas Chemical		
Joplin, Missouri	Operational	360 (400)
Beker		
Conda, Idaho	Operational	260 (290)
Carlsbad, New Mexico	Idle (1977)	460 (500)
Borden		
Geismar, Louisiana	Operational	900 (1,000)
Car-ren		
Columbus, Mississippi	Operational	180 (200)
CF Industries		
Terre Haute, Indiana	Operational	400 (440)
Donaldsonville, Louisiana	Operational	4,250 (4,700)
Fremont, Nebraska	Operational	128 (141)
Tunis, North Carolina	Operational	561 (610)
Tyner, Tennessee	Operational	454 (500)
Chemical Distributors Corp.		
Chandler, Arizona	Operational	105 (115)
Chevron		
Fort Madison, Iowa	Operational	280 (308)
Pascagoula, Mississippi	Operational	1,400 (1,500)
Richmond, California	Closed (1978)	290 (320)
Columbia Nitrogen		
Augusta, Georgia	Operational	1,400 (1,500)
Augusta, Georgia	Closed (1978)	310 (350)
Cominco (Camex)		
Borger, Texas	Operational	1,070 (1,200)

(continued)

Table A-1. (Continued)

Company, location	Status	Daily capacity Mg* (tons) as NH_3
Diamond Shamrock		
Dumas, Texas	Operational	430 (470)
Dow		
Freeport, Texas	Operational	307 (340)
Du Pont		
Beaumont, Texas	Operational	910 (1,000)
Victoria, Texas	Operational	270 (300)
Belle, West Virginia	Closed (1978)	825 (906)
El Paso		
Odessa, Texas	Operational	280 (310)
Enserch (Nipak)		
Kerens, Texas	Idle (1978)	320 (350)
Pryor, Oklahoma	Idle (1978)	270 (300)
Esmark (Swift Chemical)		
Beaumont, Texas	Idle (1978)	725 (800)
Empire Nitrogen (Georgia Nit.)		
Gordon, Georgia	Idle (1978)	90 (100)
Farmland		
Fort Dodge, Iowa	Operational	560 (620)
Dodge City, Kansas	Operational	560 (620)
Lawrence, Kansas	Operational	910 (1,000)
Pollock, Louisiana	Operational	1,120 (1,240)
Hastings, Nebraska	Operational	380 (420)
Enid, Oklahoma	Operational	2,250 (2,470)
Felmont Oil		
Olean, New York	Operational	230 (250)

(continued)

Table A-1. (Continued)

Company, location	Status	Daily capacity Mg* (tons) as NH_3
First Mississippi		
Fort Madison, Iowa	Operational	975 (1,070)
FMC		
S. Charleston, West Virginia	Operational	65 (70)
Gardinier		
Tampa, Florida	Operational	325 (360)
Georgia Pacific		
Plaquemine, Louisiana	Operational	525 (575)
Goodpasture		
Dimmitt, Texas	Idle (1978)	65 (75)
Dimmitt, Texas	Operational	105 (120)
W.R. Grace		
Big Spring, Texas	Closed (1978)	270 (300)
Memphis, Tennessee	Operational	910 (1,000)
Green Valley		
Creston, Iowa	Operational	90 (100)
Gulf & Western (N.J. Zinc)		
Palmerton, Pennsylvania	Operational	90 (100)
Hawkeye		
Clinton, Iowa	Operational	370 (400)
Hercules		
Louisiana, Missouri	Operational	190 (200)
IMC		
Sterlington, Louisiana	Idle (1978)	920 (1,000)
Sterlington, Louisiana	Operational	1,100 (1,200)

(continued)

Table A-1. (Continued)

Company, location	Status	Daily capacity Mg* (tons) as NH_3	
Jupiter			
Lake Charles, Louisiana	Operational	320	(350)
Kaiser			
Savannah, Georgia	Idle (1979)	122	(135)
Savannah, Georgia	Operational	265	(290)
Mississippi Chemical			
Pascagoula, Mississippi	Operational	470	(510)
Yazoo City, Mississippi	Operational	1,050	(1,160)
Monsanto			
Luling, Louisiana	Operational	2,270	(2,500)
N-Ren			
E. Dubuque, Illinois	Operational	640	(700)
Hobbs, New Mexico	Operational	180	(200)
Pryor, Oklahoma	Operational	250	(275)
Plainview, Texas	Closed (1977)	140	(160)
Occidental (Hooker)			
Hanford, California	Idle (1978)	100	(105)
Lathrop, California	Idle (1979)	320	(350)
Taft, Louisiana	Operational	240	(265)
Tacoma, Washington	Operational	65	(70)
Plainview, Texas	Closed (1979)	135	(150)
Oklahoma Nitrogen (Grace)			
Woodard, Oklahoma	Operational	1,100	(1,200)
Olin			
Lake Charles, Louisiana	Operational	1,300	(1,440)
Pennwalt			
Portland, Oregon	Operational	21	(23)

(continued)

Table A-1. (Continued)

Company, location	Status	Daily capacity Mg* (tons) as NH_3	
Phillips Petroleum			
Beatrice, Nebraska	Operational	560	(620)
Pasadena, Texas	Idle (1977)	680	(750)
Phillips Pacific			
Finley, Washington	Operational	410	(450)
PPG			
New Martinsville, W. Virginia	Operational	135	(150)
Reichhold			
St. Helens, Oregon	Operational	240	(260)
Rohm & Haas			
Deer Park, Texas	Closed (1978)	115	(125)
Simplot			
Pocatello, Idaho	Operational	290	(320)
Tenneco			
Pasadena, Texas	Idle (1978)	530	(480)
Terra			
Port Neal, Iowa	Operational	560	(610)
Tipperary			
Lovington, New Mexico	Closed (1979)	260	(290)
Triad			
Donaldsonville, Louisiana	Operational	910	(1,000)
TVA			
Muscle Shoals, Alabama	Operational	200	(220)

(continued)

Table A-1. (Concluded)

Company, location	Status	Daily capacity Mg* (tons) as NH_3
Union Oil		
Kenai, Alaska	Operational	2,700 (3,000)
Brea, California	Operational	750 (820)
USA Petrochem		
Ventura, California	Operational	130 (150)
U.S. Steel		
Cherokee, Alabama	Operational	470 (520)
Clairton, Pennsylvania	Operational	910 (1,000)
Geneva, Utah	Operational	185 (200)
Valley Nitrogen		
Helm, California	Closed (1978)	440 (485)
Hercules, California	Idle (1977)	185 (200)
El Centro, California	Operational	560 (620)
Vistron		
Lima, Ohio	Operational	1,270 (1,400)
Vulan Materials		
Wichita, Kansas	Closed (1978)	90 (100)
Wycon		
Cheyenne, Wyoming	Operational	450 (500)

*One megagram (Mg) equals 1000 metric tons.

Table A-2. AMMONIA PLANTS CLOSED[a]

Company	Location	Capacity[b] (TPY)
Allied Chemical	Southpoint, OH	240,000
Amoco (American Oil)	Texas City, TX	200,000
Apache	Curtiss, AZ	15,000
Beker Industries	Carlsbad, NM	210,000
Standard (Chevron Chemical)	Richmond, CA	130,000
Columbia Nitrogen	Augusta, GA	122,000
Du Pont	Belle, WVA	340,000
Duval	Hanford, CA	42,000
Estech Chemical	Beaumont, TX	300,000
Ampro (First Miss.)	Donaldsonville, LA	400,000
Goodpasture	Dimmit, TX	31,000
W.R. Grace	Big Springs, TX	100,000
IMC	Sterlington, LA	370,000
Kaiser	Savannah, GA	50,000
N-REN	Plainview, TX	60,000
Enserch (Nipak)	Kerens, TX (sold, Marsco) Pryor, OK (sold, Kaiser)	115,000 105,000
Occidental	Lathrop, CA Plainview, TX	160,000 52,000
Phillips	Pasadena, TX	230,000

(continued)

Table A-2. (Concluded)

Company	Location	Capacity[b] (TPY)
Rohm & Haas	Deer Park, TX	45,000
Tenneco	Pasadena, TX	210,000
Tipperary	Lovington, NM	100,000
Valley Nitrogen	Hercules, CA (sold to Hercules Properties)	70,000
	Helm, CA	176,000
Vulcan Materials	Wichita, KA	35,000
		3,936,000

[a]List provided by Karl Johnson, Vice President, The Fertilizer Institute, and checked with TVA February 28, 1980.

[b]Capacity is "nameplate" or equivalent. The above total is 16.0 percent of U. S. capacity, 24.8 million tons in 1980 as reported by TVA.

Table A-3. LOCATION OF SYNTHETIC AMMONIA FACILITIES BY STATE

State	Number of facilities
Texas	17
Louisiana	15
California	8
Iowa	6
Oklahoma	5
Mississippi	4
Nebraska	4
Georgia	3
Kansas	3
New Mexico	3
West Virginia	3
Alabama	2
Arizona	2
Arkansas	2
Florida	2
Idaho	2
Missouri	2
Ohio	2
Oregon	2
Pennsylvania	2
Tennessee	2
Washington	2
Alaska	1
Illinois	1
Indiana	1
New York	1
North Carolina	1
Utah	1
Virginia	1
Wyoming	1

APPENDIX B. HISTORICAL DEVELOPMENT

Between 1830 and the turn of the century, the requirements for fixed nitrogen were satisfied by imports of nitrate from Chile (Appl, 1978). Around the turn of the century, Wilhelm Ostwald offered BASF a process that synthesized ammonia by passing nitrogen and hydrogen over a metallic iron catalyst. Experimental errors produced the false impression that the process did not work, however, and interest turned to the cyanamide process (Appl, 1978; Lyon, 1975), in which ammonia is synthesized as follows:

$$CaO + 3C \xrightarrow[2000^{o}C]{} CaC_2 + CO$$

$$CaC_2 + N_2 \xrightarrow[1000^{o}C]{} CaCN_2 + C$$

$$CaCN_2 + 3H_2O \rightarrow CaCO_3 + NH_3$$

Energy consumption was 190 GJ per metric ton. In another approach, the electric arc process, air was passed over an electric arc which raised the temperature to $3000^{o}C$ and produced NO_2, at a penalty of 700 GJ per metric ton. Frits Haber finally succeeded in synthesizing ammonia using an osmium catalyst. While others, such as Nernst, were attempting to produce high conversion, Haber's approach was to pursue high reaction rate with internal process recycle at high pressure.

Carl Bosch in 1909 was given the job of extending Haber's laboratory results to commercial scale. He succeeded in developing an inexpensive, efficient catalyst (which is essentially unchanged to this day) and in developing suitable equipment for high-pressure synthesis. In 1913, a 30 TPD plant in Oppau (near Karlsruhe) began operation. Virtually all the world's ammonia production is based on this technology.